Probing Magnetic Excitations in Co(II) Single-Molecule Magnets by Inelastic Neutron Scattering

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Supporting Information

"M_S = ±1/2 ($\phi_{1,2}$) → ±3/2 ($\phi_{3,4}$)" Transition in 1-d_{18} Probed by Variable-Field INS

As indicated in the text, the signal/noise ratio of the data collected at DCS below prevents a conclusive assignment. The data are provided for completeness.

Both magnetic and phonon peaks are allowed in INS, both contribute to the observed peaks. Magnetic scattering is more prominent at small scattering-vector |***Q***|, whereas phonon scattering prevails at high |***Q***|.[1] It should be noted that INS experiments using a 10 T magnet at DCS are particularly challenging, as the magnet blocks a large portion of the detectors, leading to low signal/noise ratios of the peaks.

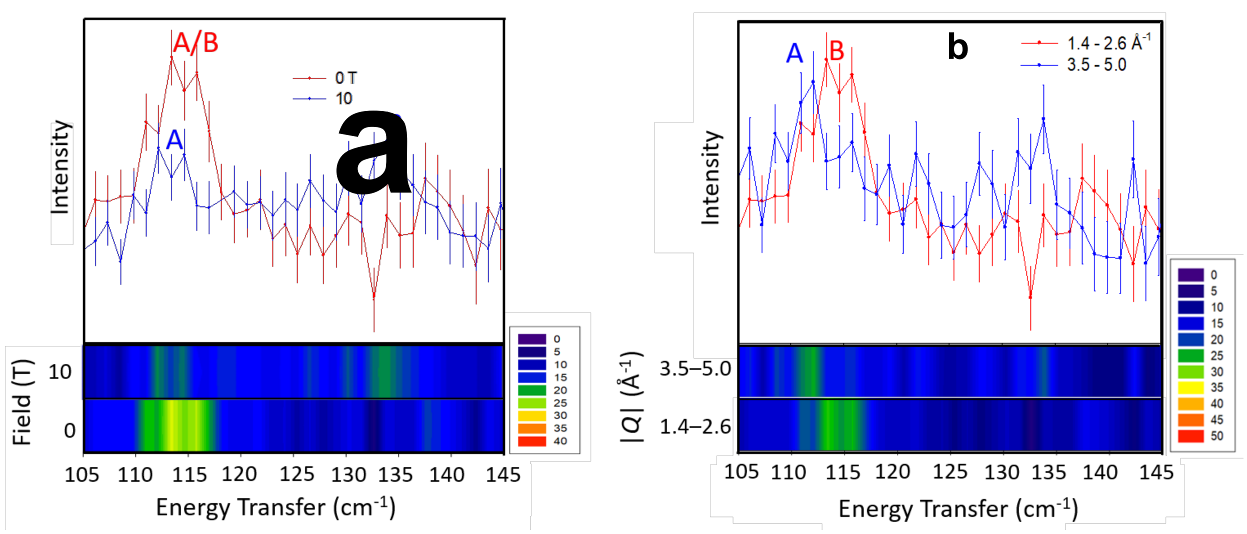
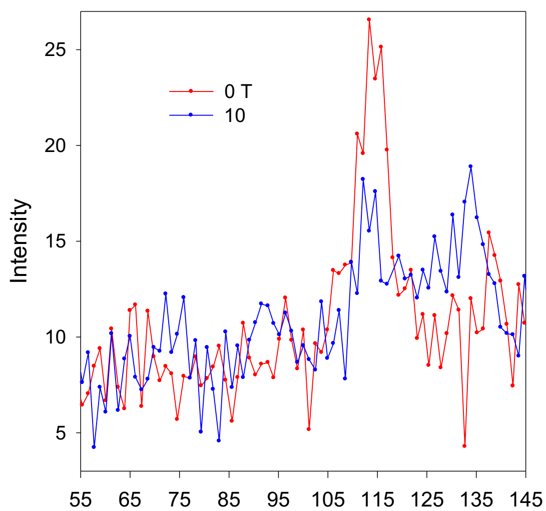


Figure S1. (a) Variable-field INS spectra of **1-*d*18** at 0 and 10 T at small |***Q***| (1.4 Å^{-1} – 2.6 Å^{-1}). Contour plots provide a comparison of peak intensities at 0 T and 10 T. (b) 0 T INS spectra at small |*Q*| (1.4 Å^{-1} – 2.6 Å^{-1}) and large |*Q*| (3.5 Å^{-1} – 5.0 Å^{-1}). Contour plots provide a comparison of peak intensities at small and large |***Q***|. Alternative plot of Figure 6a and its discussions are given in SI/S4-1. Analyses of the signal/noise ratios for the peaks in the figure are given in Table S1.

Figure S1a, at small |***Q***|, appears to highlight the magnetic features. At 0 T, the overlapping peaks A and B at 113 cm^{-1} are more intense. At 10 T, B shifts to ~134 cm^{-1} (Figure S1a-contour plot). This observation is consistent with those in Raman and far-IR.[2] |***Q***| dependence of the A/B peak at 113 cm^{-1} (Figure S1b) is consistent with the nature of A and B at 0 T. At low |***Q***|, B is dominant, indicating it is mostly magnetic. At larger |***Q***|, B mostly disappears and largely phonon A is prominent. An alternative plot of Figure S1a is given below, with error analyses of the peaks in Table S1.



Alternative plot of Figure S1a. Variable-field INS data for **1-*d*$_{18}$** at 0 T and 10 T with |***Q***| summed between 1.4 Å^{-1} – 2.6 Å^{-1}. There is no alternative plot for Figure S1b.

Table S1. Signal/noise ratios for the peaks in Figure S1

	0 T peak at ~115 cm^{-1}		**10 T peak at ~135 cm^{-1}**	
	Noise	**Signal**	**Noise**	**Signal**
Mean	8.5(1.7)	19.3(5.4)	8.4(1.9)	14.8(2.6)
Signal/noise ratio	2.3		1.8	

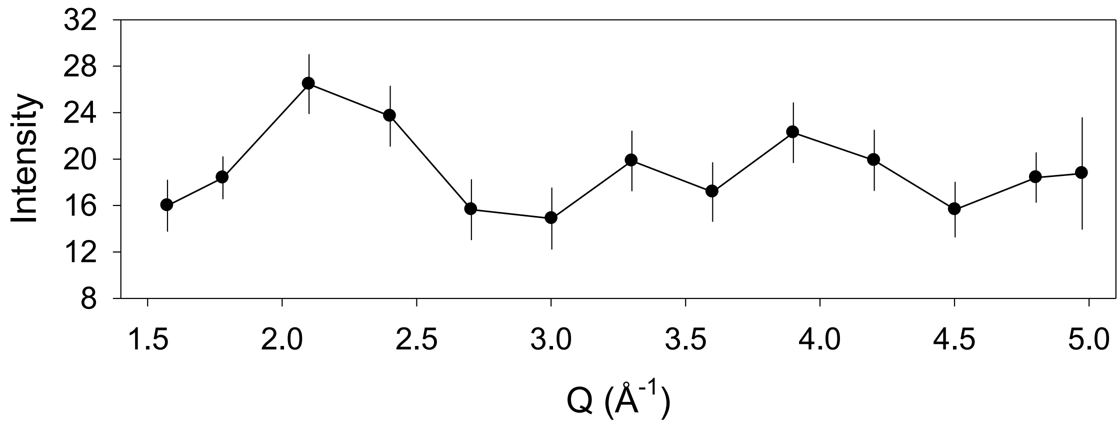
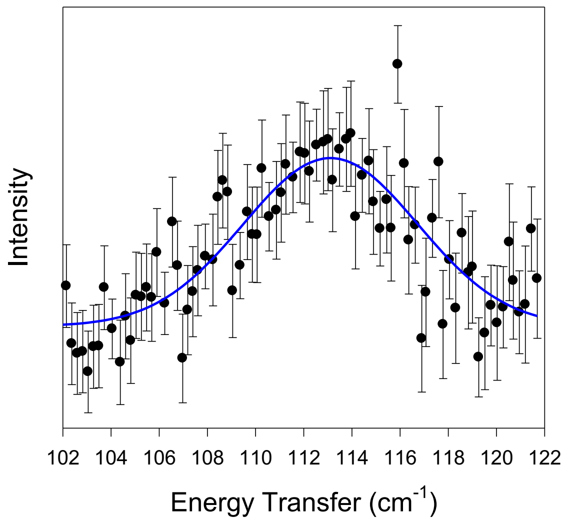


Figure S2. |***Q***| dependence of 113 cm^{-1} peak at 0 T.

The |***Q***| dependence of the 113 cm^{-1} peak in INS at 0 T is shown in Figure S2. The data seem to suggest this inter-Kramers doublet transition is not purely magnetic, as the intensity does not decrease as |***Q***| increases. This transition is also not purely a phonon since it does not increase by |***Q***|^2 as |***Q***| increases. The |Q| dependence is relatively constant throughout the studied |***Q***| range. Because it neither consistently increases nor decreases with |***Q***|, we consider this peak to be a coupled spin-phonon excitation.

Error analysis of the 113 cm^{-1} peak is in Figure S1 is given below.



Area	65(1)
Center	113.0(3) cm^{-1}
Full-width half-maximum	8(1) cm^{-1}
Background	8.4(5)

Figure S3. Error analysis of the 0 T spin-phonon coupled peak of **1-*d*$_{18}$** at 113.0(9) cm^{-1} by DCS. The |*Q*| range is summed over all *Q* and the step size is 0.24 cm^{-1}. Error bars indicate one standard deviation. Error analysis:

$\sigma_{\text{total}}{}^2 = \sigma_{\text{random}}{}^2 + \sigma_{10\%\text{*FWHM}}{}^2 = 0.3^2 + 0.8^2 = 0.73$; $\sigma_{\text{total}} \approx 0.9$ cm^{-1}.

With the addition of the 10 T magnet to the sample environment at DCS, there is a degradation by a factor of 2.5 in the incident beam size in comparison to the normal, full beam. In addition, there is background contribution from the small aperture of the magnet and shadowing of detectors by the magnet, giving ~33% detector efficiency.

References for Supporting Information

[1] A. Furrer, J. Mesot and T. Strässle, *Neutron Scattering in Condensed Matter Physics*, World Scientific, **2009**, p.

[2] D. H. Moseley, S. E. Stavretis, K. Thirunavukkuarasu, M. Ozerov, Y. Cheng, L. L. Daemen, J. Ludwig, Z. Lu, D. Smirnov, C. M. Brown, M. Atanasov, E. Bill, F. Neese, A. Pandey, A. J. Ramirez-Cuesta, A. C. Lamb and Z.-L. Xue, *Nat. Commun.* **2018**, *9*, 2572.